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A Survey on Research Needs on Personal Samplers for Toxic Organic Compounds

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A SURVEY ON RESEARCH NEEDS ON PERSONAL SAMPLERS FOR TOXIC ORGANIC COMPOUNDS

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FOREWORD

This report is one of a series of reports designed to provide information on the development of Standard Reference Materials and measurement methods in support of quality assurance for environmental monitoring. The National Bureau of Standards and the Environmental Protection Agency have entered into an interagency agreement to coordinate the standards and measurement services activities of NBS with the quality assurance programs of EPA. Reports of work carried out under this agreement will appear in the EPA Environmental Monitoring Research Report Series.

Under this agreement, NBS will develop and provide, as directed by EPA,

- Standard Reference Materials
- Improved or new measurement methods
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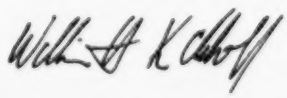
- Calibration standards and protocols

as well as other services deemed necessary for assuring the accuracy and reliability of environmental monitoring data. Standard Reference Materials developed under this agreement will be available for purchase from the NBS Office of Standard Reference Materials. Work under this agreement is coordinated by the Office of Monitoring Systems and Quality Assurance in EPA and by the Office of Environmental Measurements in NBS and questions concerning this program should be addressed to the Office of Environmental Measurements, National Bureau of Standards, Washington, DC 20234.



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ABSTRACT

A survey is presented on the research and development needs for personal monitoring devices for toxic organic compounds in the ambient atmosphere. This survey includes a description of organic compounds and their ambient concentrations in the atmosphere, individual compounds of high priority, a summary of a literature survey, a description of commercially available workplace samplers, a summary of recent developments in ambient personal monitoring and recommendations on major research needs. The high priority compounds identified were predominately volatile chlorinated organics and consist of the following compounds: methyl chloride, dichloromethane, benzene, carbon tetrachloride, chloroform, dichlorobenzenes, 1,2-dichloroethane, methyl chloroform, trichloroethylene and perchloroethylene. The literature survey covers the period, 1974-79, and describes sorbent materials for organic sampling, analytical procedures, and developments on personal monitoring devices. The literature is predominately concerned with personal sampling in the workplace environment. Commercially available personal samplers described are Dupont's Pro-Tek organic vapor badge, Abcor's gasbadge, 3-M's organic vapor monitor and the Minimonitor (P. W. West, Louisiana State University). Recent activities include a description of an EPA sponsored program at Monsanto Research Corporation on development of personal samplers for organics in the ambient atmosphere. Monsanto has developed an active sampler consisting of a miniature pump with three sorbents in series - Tenax GC, Poropak-R and Ambersorb XE-349. A description is also given of several recent field studies on sampling and analysis for benzene and chlorinated hydrocarbons in the ambient atmosphere. The survey concludes with recommendations for research and development activities in the following areas: evaluation of sorbent materials, development of analytical techniques based on electron capture-gas chromatography, evaluation of available active and passive samplers on the high priority compounds, development of passive samplers and development of standard mixtures for evaluation and calibration of personal exposure devices.

CONTENTS

Foreword iii

Abstract iv

Tables vi

1. Introduction 1

2. Organic Compounds in the Atmosphere 2

3. Monitoring Needs 4

4. Survey of Organic Personal Exposure Devices 11
   Summary of the Literature 11
   Commercially Available Samplers 14
   Conclusions 16

5. Summary of Recent Activities 17

6. Recommendations for Research and Development Activities . . 20

References 23

TABLES

Number		Page
1	Organic Compounds in the Atmosphere	3
2	General Sorption-desorption Systems for Organic Compounds . . .	8
3	TSCA Priority List	10
4	Volatile Organic Compounds of Atmospheric Concern	13

SECTION 1

INTRODUCTION

Regulatory decisions on air pollution control, which involve direct and indirect costs of billions of dollars, should be based on an adequate knowledge of the health impacts of air pollution. A weak link in health effects studies is our knowledge of individual exposures. The importance of population exposure estimates in air pollution health effects studies makes it imperative that future studies include estimates more representative of what people breathe. Studies of air pollution health effects have usually relied on one or several fixed monitoring stations to provide data for an estimate of the exposure received by an entire neighborhood. Epidemiologists have begun to call for something better. Several recent meetings of specialists in the field of air pollution health effects have led to recommendations urging the prompt development of small, portable individual air pollution monitors (1).

In response to this need and under a EPA-NBS Interagency Agreement, the NBS program is to develop principles and concepts and actual devices for determining personal exposure to critical air pollutants. Both passive and active monitors will be developed to provide long-term integrated exposures (> 24 hours) and data on short-term exposure events (< 1 hour). During the first year of the program the pollutants EPA has identified as having the highest priority are fine particulates, nitrogen dioxide and toxic organics.

Because limited information for personal exposure devices for toxic organics was available at the beginning of this program, the work reported here is a survey of the research needs and promising approaches for developmental activities.

In the following discussion we will present a description of the classes of organic compounds present in ambient air and typical concentration levels, monitoring needs as perceived from regulations and agency programs, a summary of a literature survey, a description of commercially available workplace devices, a summary of some recent activities on personal exposure devices for ambient organics and recommendations of major research needs in this field.

SECTION 2

ORGANIC COMPOUNDS IN THE ATMOSPHERE

Organic compounds are emitted into the atmosphere as a result of biogenic and anthropogenic activities. The most abundant single organic compound in the atmosphere, methane (CH_4), results predominantly from microbiological processes, e.g., dead plant decay, and has a natural tropospheric background concentration of ca. 1.4 ppm. Another major natural class of organic component is the terpenes, which are emitted by many living plant species. Other known natural gaseous organic compounds in the atmosphere include organic mercaptans and sulfides and methyl iodide (2). Many of the other organic compound emissions into the atmosphere are a result of anthropogenic activities. A major source is motor vehicle emissions with other significant contributions from stationary fuel combustion, solvent evaporation, solid waste disposal, gasoline marketing and forest fires (2). Thus the major urban anthropogenic organic class is hydrocarbons, of which the total concentration may range from background (ca. 1.4 ppm) up to a few parts per million by volume.

The presence of anthropogenic hydrocarbons in the atmosphere may contribute to adverse environmental consequences. The non-methane hydrocarbons (NMHC) are reactive in the presence of solar radiation and oxides of nitrogen (from combustion in mobile and stationary sources) and promote elevated levels of tropospheric ozone (O_3) and photochemical smog (3,4). Halogenated hydrocarbons, in particular the freons, are so stable in the lower atmosphere that they accumulate and diffuse into the stratosphere. Their photodegradation products destroy O_3 and these compounds thus may pose a long-term threat to the protective stratospheric O_3 layer (5-8). Other organic compounds are of concern because they pose a direct toxic threat when inhaled. For example, emissions of vinyl chloride (9) and benzene (10) are controlled by federal regulation because of the demonstrated health effects of these compounds (11-13).

A detailed compilation of organic compounds, with ranges of concentration known to be present in the polluted troposphere, has been given in the excellent monograph by Graedel (14). The classes of compounds compiled include hydrocarbons, carbonyl compounds, oxygenated organic compounds, nitrogen-containing organic compounds, sulfur-containing organic compounds, organic halogenated compounds and organometallic compounds. Table 1 shows some of these classes and their more prominent members with ranges of concentration.

TABLE 1. CHEMICAL COMPOUNDS IN THE ATMOSPHERE AND AMBIENT CONCENTRATIONS.

Name	Concentration	Name	Concentration
Alkanes (total)	1400 - 6000 ppb	Acrolein	1 - 13 ppb
Methane	1300 - 4000 ppb	Acetone	0.08 - 6.8 ppb
Ethene	0.7 - 700 ppb	Formic Acid	4 - 72 ppb
Terpenes (total)	0.1 - 1 ppb	Esters (total)	1 - 100 ppb
Cyclic Hydrocarbons (total)	2 - 50 ppb	Quinones	<0.001 - 0.02 ppb
Cyclohexane	3 - 6 ppb	Methanol	8 - 100 ppb
Toluene	0.005 - 129 ppb	Phenol	2.8 ppb
Benzene	0.025 - 57 ppb	Halogen Compounds	0.8 - 3.0 ppb
m-Xylene	1 - 61 ppb	Methyl Chloride	0.8 - 2.2 ppb
Naphthalene	<0.001 - 0.06 ppb	Chloroform	0.004 - 0.25 ppb
Pyrene	<0.001 - 0.02 ppb	Carbon Tetrachloride	0.001 - 0.26 ppb
Benzo[a]pyrene	<0.001 - 0.008 ppb	Trichloroethylene	0.01 - 0.35 ppb
Aldehydes + Ketones (total oxygen compound)	1 - 200 ppb	Vinyl Chloride	.005 ppb
Formaldehyde	1 - 160 ppb	Halogenated Aromatics	∿ 0.08 ppb
		Cyanogen	10 - 20 ppb
		Sulfur Compounds	4 ppb

SECTION 3

MONITORING NEEDS

It is obvious from the discussion in Section 2 above that there is a wide variety of classes of organic compounds with many individual members present in a polluted atmosphere. These compounds represent a wide range of volatilities, polarities, and functionalities-properties which will surely determine the choice of the sampling medium for a given compound or class of compounds. In addition, the analytical work-up will vary for different classes of compounds with different chemical and physical properties. Finally, the most important factor to consider in determining monitoring needs is the potential health threat, a factor which may range from none to acute over the range of compounds found in the atmosphere. The potential health threat of an organic compound is in turn determined by its degree of toxicity, carcinogenicity or mutagenicity, production rate, emission rate into the atmosphere, and its atmospheric persistence or lifetime.

In order to begin a program on development of personal exposure devices, the identification of a finite set of organic compounds (classes) of high priority based on potential health threat is required. Once this set of compounds is identified, candidate sampling methods and analytical work-ups can be chosen for development and evaluation. Our approach in identifying high priority monitoring needs has been to a) examine federal regulations relative to toxic organics in the atmosphere; b) survey documented information on high priority toxic organics and c) consult with EPA personnel on high priority agency programs on toxic organics.

The EPA is the federal agency with responsibility for the control of emissions of toxic organics into the atmosphere. The EPA has several regulatory options available to carry out congressionally mandated emission control. The Clean Air Act (15) as amended by the Clean Air Amendments (CAA) of 1970 and 1977 provides several options for control. Those options which have resulted in regulations on organic compounds include 1) National Ambient Air Quality Standards (NAAQS)/State Implementation Plans; 2) National Emission Standards for Hazardous Air Pollutants, 3) New Source Standards of Performance and 4) National Emission Standards for Mobil Sources.

Another major piece of legislation relative to control of organic compounds in the environment is the Toxic Substances Control Act (TSCA) of 1976 (16). The TSCA enables EPA to gather from industry the required information on any organic chemical produced as needed to determine its potential for damaging human health and the environment, and to control them where necessary to protect the public.

THE CLEAN AIR ACT

Section 109 of the Clean Air Act requires that the Administrator set national primary and secondary ambient air quality standards. Primary standard indicates those levels of air quality, including an adequate margin of safety, which are necessary to protect public health. Secondary standards indicate those levels which are necessary to protect public welfare from any known or anticipated adverse effects. Public welfare includes effects on vegetation, wildlife, physical properties of the atmosphere, materials, etc. NAAQS have been set for particulate matter, sulfur oxides, nitrogen oxides, photochemical oxidants, non-methane hydrocarbons (NMHC), and carbon monoxide (17).

Standards are based on information from air quality criteria documents prepared in accordance with section 108 of the Act. In addition, for each criteria pollutant (a pollutant for which NAAQS are established), EPA must prepare a document relating control techniques and costs of control. A pollutant is considered a likely candidate for NAAQS if:

1. there is an adverse effect on public health or welfare caused by the presence of the pollutant in the ambient air, and

2. the presence of the pollutant in the air is the result of numerous and diverse mobile and stationary sources.

To insure that levels indicated by NAAQS are attained, section 110 of the Act requires States to submit Implementation Plans which demonstrate procedures for attaining these standards. State plans must provide for attaining primary standards within three years (a two-year extension may be requested), and secondary standards within a reasonable time after approval of such a plan.

The only regulation for organics under the NAAQS is on NMHC, i.e., total hydrocarbon minus methane. It should be noted that although a standard exists for NMHC, routine monitoring for NMHC is done in practice infrequently because such a measurement is difficult to do accurately at ambient levels and because the NMHC, as a class, is not directly associated with adverse health effects. Rather the NMHC promotes the formation of O_3 and other toxic components of photochemical smog.

A potentially more important section of the Clean Air Act for the regulation of organics is section 111, in particular 111(d). This section requires EPA to set standards of performance on new or modified stationary sources for any non-criteria air pollutant "which may reasonably be anticipated to endanger health or welfare".

Section 112 of the Act requires EPA to identify pollutants which cause an increase in mortality or an increase in serious irreversible, or incapacitating reversible illness. These pollutants are generally considered to be less ubiquitous pollutants covered by the NAAQS.

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For any pollutant which is considered hazardous, EPA must establish emission standards which provide an ample margin of safety to protect public health. In general, standards will be established by defining ambient guideline concentrations of a pollutant which provide an ample margin of safety to protect health. Dispersion models are then used to determine the allowable emissions that will ensure that the ambient guideline concentrations are not exceeded. As presently written, the Act does not permit consideration of cost or availability of demonstrated control technology in determining allowable emissions. Hazardous emission standards have presently been promulgated for the inorganics-mercury, asbestos, arsenic and beryllium and for the organics-vinyl chloride (9) and benzene (10).

Section 202 of the Act requires the Administrator to set emission standards for any air pollutant coming from a motor vehicle if the pollutant is harmful to public health and welfare. Mandatory emission reductions for CO, total hydrocarbon (HC), and NO_x were written into the Act for light duty vehicles. The Act required a 90 percent reduction in NO_x ($NO+NO_2$) to be effective in 1976. These deadlines were subsequently extended to allow vehicle manufacturers additional time to develop control systems.

In summary under the CAA, the only present regulations on organic compounds are for NMHC under the NAAQS, for vinyl chloride and benzene as hazardous pollutants, and for total hydrocarbons from vehicular emissions. Of these only vinyl chloride and benzene are associated with direct health effects and therefore should be considered with regard to personal monitoring needs. It should be mentioned at this point that West (18,19) has developed a permeation type, personal sampler for vinyl chloride.

THE TOXIC SUBSTANCES CONTROL ACT (TSCA)

The TSCA of 1976 is a comprehensive piece of legislation designed to provide the information required to assess the potential health or environmental threat from chemical substances. The TSCA also provides EPA with the means for regulating the production, distribution, use and disposal of chemical substances when deemed necessary. A good summary of TSCA may be found in reference (20). We only discuss here that aspect of the law which provides information on toxic organics, which may be subject to regulation and which may present needs for personal monitoring.

Section 4 on the "Testing of Chemical Substances and Mixtures" is pertinent to this discussion. Under this section EPA may require manufacturers or processors to provide the test data required to determine whether chemicals pose potential threats to health or the environment. Test data may be required to characterize chemical substances in terms of their environmental persistence and toxicity and to assess health and environmental effects including carcinogenic, mutagenic, teratogenic, behavioral and synergestic effects.

Section 4(e) establishes an Interagency committee to develop a "Priority List" of chemicals to which EPA should give priority consideration for promulgating rules for obtaining test data. Among the relevant factors the committee must consider in recommending this list are the following: 1) the

quantity of the chemical substance manufactured; 2) the quantity which may enter the environment; 3) the extent of human exposure to the chemical substance, and 4) the existence of data on the effects of the substance on health and the environment.

The third factor is particularly important here in that it implies the need for personal exposure studies. The Priority List may contain up to 50 chemical substances. The fourth report of this interagency committee to EPA lists the latest Priority List of chemicals. This list of 33 individual compounds or classes of compounds is reproduced in Table 2. It is of interest to note that of these 33 substances, 30 are organic compounds or classes of compounds.

While we regard the TSCA Priority List to be the comprehensive source in identifying monitoring needs for specific organics or classes, some other sources of information were examined. The Monsanto Corporation has recently conducted a study for EPA which resulted in the identification of 20 high priority atmospheric carcinogens from a list of 125 high volume chemicals having the potential of becoming airborne pollutants (21). This prioritization was based on a rating scale which for each compound included the emission rate, the atmospheric persistence and the potency relative to benzo-(a)pyrene.

The chemicals on the list in a prioritized ranking are: benzo(a)pyrene, tetrachloroethylene, ethylene dichloride, benzene, carbon tetrachloride, ethylene dibromide, toluene-3,4-diamine, dioxane, acrylonitrile, ethylenimine, benzyl chloride, benzidine, pentachlorophenol, dichloropropene, styrene, hexachlorobutadiene, di-(2-ethylhexyl)phthalate, vinyl acetate, ethylene oxide, and acrolein.

Both the TSCA Priority List and the Monsanto list include toxic compounds of concern, whether their release into the environment occurs through the aqueous, terrestrial or atmospheric media. We are concerned here about organic substances which are released into and may persist in the atmosphere. We are further concerned here for personal monitoring needs for vapor phase organics in the atmosphere. Many of the toxic organics on the previous lists would occur in the particulate phase if they persist in the atmosphere e.g., benzo(a)pyrene. A separate task of this same Interagency Agreement is concerned with the personal sampling and analysis of pollutants in the particulate phase. Therefore, these lists were culled to eliminate those compounds with low vapor pressure or high atmospheric reactivity with the OH radical or O_3. The upper limit chosen for vapor pressure was the boiling point (ca. 180 °C) of the dichlorobenzenes, which have actually been observed in field studies as discussed below.

For atmospheric reactivity, compounds with a half-life less than one week based on reaction with OH radicals were eliminated. A mean tropospheric OH concentration of 5×10^5 molecules/cm^3 was chosen and the rate constants were taken from the recent review of Atkinson (22). The choice of one week is somewhat arbitrary, but it does provide a clean dividing line between the chlorinated compounds and the other organics, with the exception of benzene. For example, toluene and the cresols have half-lives of 3.8 and 0.5 days,

TABLE 2. TSCA PRIORITY LIST

Acetonitrile
Acrylamide
Alkyl epoxides
Alkyl phthalates
Aniline and bromo, chloro and/or nitroanilines
Antimony (metal)
Antimony sulfide
Antimony trioxide
Aryl phosphates
Chlorinated benzenes, mono and di-
Chlorinated benzenes, tri, tetra and penta-
Chlorinated naphthalenes
Chlorinated paraffins
Chloromethane
Cresols
Dichloromethane
1,2-Dichloropropane
Cyclohexanone
Glycidol and its derivatives
Halogenated alkyl epoxides
Hexachloro-1,3-butadiene
Hexachlorocyclopentadiene
Isophorone
Mesityl oxide
4,4-Methylenedianiline
Methyl ethyl ketone
Methyl isobutyl ketone
Nitrobenzene
Polychlorinated terphenyls
Pyridine
Toluene
111-trichloroethane
Xylenes

respectively, whereas methyl chloride and carbon tetrachloride have half-lives of 1.6 years and greater than 65 years, respectively. Benzene is included on this criterion in that its half-life is 16.5 days. If the criterion chosen had been 1 day instead of 7, a few additional compounds, such as toluene and methyl isobutyl ketone (τ = 1.7 days), would have been included but not many.

Rate data with OH were not available for some of the compounds and most of these were compounds on the Monsanto list containing the vinyl grouping. A reaction half-life of 10 days with O_3 was estimated for these compounds using $10^{-18} cm^3 s^{-1}$ for the rate constant (23) and a mean urban O_3 concentration of $10^{12} cm^{-3}$ (0.05 ppm). Since it is highly probable that the reaction half-life with OH is less than that with O_3, these compounds were not included. A few compounds remained with no OH or O_3 rate data (e.g., acetonitrile, pyridine and ethylene oxide) but these were not included because of their probable atmospheric reactivity.

The remaining compounds are shown in columns 1 and 2 of Table 3. This table also lists two other sets of toxic organics which are based on current EPA programs. Column 3 lists nine organic compounds found at elevated concentrations during a recent EPA field survey in four different urban areas, New Orleans, Houston, Niagara Falls, and Newark (24a). These compounds are included in an extensive 3-year study--The Total Exposure Assessment Methodology (TEAM) Study--being mounted by EPA to obtain personal exposure data (24b). Column 4 lists the eight toxic organic compounds for which EPA has requested that NBS provide gas standards under a separate task of this same Interagency Agreement.

There are two obvious conclusions which can be drawn from this Table. The first is that there is considerable overlap among these lists of high priority organic compounds. The second is that the Table predominately consists of low molecular weight, halogenated organic compounds.

TABLE 3. VOLATILE ORGANIC COMPOUNDS OF ATMOSPHERIC INTEREST

TSCA[a]	MONSANTO[b]	EPA[c] FIELD STUDY	ORGANIC[d] STANDARDS
	Benzene	Benzene	Benzene
	Carbon Tetrachloride	Carbon Tetrachloride	Carbon Tetrachloride
Methyl Chloride			
		Chloroform	Chloroform
Mono/dichlorobenzenes		Dichlorobenzenes	
Dichloromethane			
		1,2-dichloroethane	
1,2-dichloropropane			
	Ethylene Dibromide		Ethylene Dibromide
	Ethylene Dichloride	Ethylene Dichloride	Ethylene Dichloride
Methylchloroform		Methylchloroform	
	Perchloroethylene	Perchloroethylene	Perchloroethylene
		Trichloroethylene	Trichloroethylene

[a] From TSCA Priority List.

[b] From Monsanto Priority List, Reference 21.

[c] Ubiquitous Ambient Organics Included in two EPA Field Studies, Reference 24.

[d] Organic Standards Being Prepared for EPA Under Same Interagency Agreement.

SECTION 4

SURVEY OF ORGANIC PERSONAL EXPOSURE MONITORS

SUMMARY OF LITERATURE SURVEY

A literature survey on sampling and analytical methods for detection of toxic organics at ambient levels is a part of the EPA-NBS project. Little work has been done to this date on personal exposure devices for toxic organics at ambient levels. The aim of this work is to evaluate the recent developments on performances of several sorbents as collection media for the quantitative concentration and analysis of volatile, hazardous vapor-phase compounds from the ambient atmosphere. A brief summary on commercial monitoring devices is also included.

The literature in this survey covers the five year period (1974 - 1979). It is appropriate at this point that the open literature and EPA reports on classes and ranges of concentration of hazardous organic compound present in the urban and non-urban ambient air should be considered first. The survey below discusses the solid sorbents and analytical techniques which have been used, as well as developments on sampling devices (dosimeters).

Activated carbon has been selected and used by NIOSH for collecting organic vapors (26,27). However, the detrimental effects caused by water and the reactivity of collected samples with charcoal, dictates the evaluation of alternative solid adsorbents. The criteria for the evaluation of methods for the collection of organic pollutants in air using solid sorbents is a subject of several recent papers (28,29,30), a monograph by NIOSH (31) and a recent EPA monograph (32); the analytical methods for organic pollutants have been recently discussed at length by NIOSH (33).

A recent evaluation (34) of solid sorbent materials for sampling organic vapors indicated three major classes: 1) porous polymers (e.g., Tenax-GC, Porapaks, Chromosorbs); 2) carbonaceous materials (activated carbons, charcoals, graphitized carbon black, Ambersorbs); and 3) others (e.g., molecular sieves, silica gel, liquid-coated solid supports).

The porous polymers were found (34-37) to have the most desirable properties for air sampling, having low background and low reactivity as well as high capacities for many compounds. However, the porous polymers were found to have little capacity for the more volatile compounds. The carbonaceous materials were noted to have much better capacities for volatile compounds, but are plagued with reactivity problems and susceptibility to water vapor (hydrophylicity).

The additional advantages for sampling of organic pollutants with porous polymer sorbents are high selectivity, ease of sample handling and ability to analyze polar materials not recoverable from charcoal (38); more on the subject is reported elsewhere (39-42). After a thorough evaluation of five major solid sorbents, three were selected for future consideration for use in a miniature air sampling system (34).

Tenax. The only high-temperature (400 °C) adsorbent available which allows the quantitative thermal desorption of low-volatility organic compounds.

Porapak R. One of the highest-capacity polymeric adsorbents with an overlap in range of utility with Tenax-GC.

Ambersorb XE-340. Anticipated for the desorption of compounds of intermediate volatility; more stable than charcoal towards water vapor.

By an independent study (43), Tenax-GC was found to be superior to other sorbents as a collection medium for volatile, hazardous, vapor-phase compounds from the ambient atmosphere. The effects of humidity, background air pollution, repeated re-use of sorbent, and transportation and storage of collected samples were also investigated. The general sorption-desorption systems for organic compounds in regard to the most used sorbents, desorption solvents and the types of compounds collected is summarized in Table 4. Evaluation of a technique for sampling low concentrations of organic vapors in ambient air is a topic of a recent paper (44).

Many analytical techniques have been applied to the identification and quantitation of organic compounds in ambient environmental media. In effective measurement of the ambient concentration of a toxic material in air, the following steps are involved a) collecting the sample (sorbent medium, e.g. Tenax-GC, carbon, chromosorb, etc.); b) extracting the components of interest from the sample; c) concentrating the extract, and d) injecting the sample into a gas chromatograph coupled to a suitable detector. A combined technique of capillary gas chromatography with mass spectrometry has been recently applied for analysis of air pollutants (45). A NIOSH Manual of Analytical Methods has also been published (33). A recent book (46) discusses in detail the chemistry sources, sampling and collection of air pollutants, as well as the analysis of pollutants by instrumental methods.

In 1970, the Occupational Safety and Health Administration (OSHA) developed standards to protect employees against the potentially harmful effects of approximately 400 chemicals (20,26). This set of standards is routinely reviewed and updated as more and more clinical information on the physiological impact of these chemicals became available. When these occupational standards were first published, the recommended sampling method for organic vapors was the charcoal tube method.

The charcoal tube method was originally selected by NIOSH and recommended as the referee sampling method for organic vapors (26,51,61). The method involves pumping of a known volume of air through a charcoal packed tube for a measured period of time (the charcoal serves as an adsorbent for organic vapors). The charcoal is then extracted with an appropriate solvent

TABLE 4. GENERAL SORPTION-DESORPTION SYSTEMS FOR ORGANIC COMPOUNDS.

Sorbent	Desorption Solvent	Types of Compounds
Activated carbon	Carbon disulfide dichloromethane ether (1% methanol or 5% isopropyl alcohol sometimes added)	Misc. volatile organics: methyl chloride, vinyl chloride, and other chlorinated aliphatics, aliphatic and aromatic solvents, acetates, ketones, alcohols, etc.
Silica gel	Methanol, ethanol diethyl ether, water	Polar compounds: alcohols, phenols, chlorophenols, chlorobenzenes, aliphatic and aromatic amines
Activated alumina	Water, diethyl ether, methanol	Polar compounds: alcohols, glycols, ketones, aldehydes, etc.
Porous polymers	Ether, hexane, carbon disulfide, alcohols	Wide range of compounds: phenols, acidic and basic organics, multi-functional organics, etc.
Chemically bonded and other GC packings	Ether, hexane, methanol	Specialized high boiling compounds, pesticides, herbicides, polynuclear aromatics, etc.
Thermal Desorption	None	Misc. volatile organics, halogenated organics, hydrocarbons, aromatics, etc.

(usually carbon disulfide) and the extractant analyzed with a gas chromatograph. The major disadvantage of this method is that it employs personal sampling pumps, which can weigh up to 2 pounds each.

Recently several industrial companies introduced a new type of air sampler, the passive organic vapor dosimeter, which can replace the charcoal tube. This dosimeter also relies on the ability of charcoal to selectively adsorb organic vapors, but differs in that the vapors enter the sampler by molecular diffusion or permeation rather than by mechanical means. Consequently, the dosimeter requires no electrical power. Recent emphasis has also been toward the development of portable personnel dosimeters which could be used up to eight hours to determine "time-weighted-average" (TWA) exposures. For example, current standards for vinyl chloride vapor (9,47) call for an action level of 0.5 ppm TWA exposure, which if exceeded, requires the implementation of an extensive personal monitoring program. This directive (9,47) permits a maximum allowable 8-hr TWA exposure of 1 ppm to vinyl chloride and a maximum permissible exposure of 5 ppm for no more than 15 min. A method for measuring the exposure of personnel to vinyl chloride has been developed which utilizes the permeation technique for sampling (18).

The abundant literature on the development strategy for pollution dosimetry is a subject of several papers, monographs, and books (25,32,46,48-59).

COMMERCIALLY AVAILABLE SAMPLERS

Several types of badge-size devices for monitoring individual exposure to hazardous organics at ambient concentrations now are being produced by several industrial companies. These types of samplers are passive and are worn on the clothing as small badges. By definition, a passive personal monitor is a device worn on an individual for the purpose of measuring - without the use of an active flow device - personal exposure (61). There are several advantages to passive monitors (badges); they are small, lightweight, and easily worn by any individual. The badge uses the principle of diffusion or permeation of the organic vapor through a membrane to a charcoal sorbent. The badges, however, are not without disadvantages - e.g. high humidity alters the adsorption of various organic vapors on charcoal. It is not yet apparent what can be done to correct for high humidity effects in passive monitors with charcoal sorbent (61). Commercially available passive organic samplers include DuPont's Pro-Tek badge, Abcor's gasbadge, 3-M's organic vapor monitor and the Minimonitor (P. W. West).

Recently DuPont's Applied Technology Division (62-64) introduced an inexpensive and very light (7.7 g) Pro-Tek pollution-monitoring badge for hazardous organics. The organic vapor monitoring system is designed around a small strip having 300 mg of activated charcoal contained in a rectangular envelope perforated with a known number of accurately sized pores. After activating the badge by removing impervious covers from the pores, the contaminants diffuse through the pores and are adsorbed on the charcoal. The badge can be deactivated by replacing the impervious strips. Two sampling rates, 50 cc per minute and 100 cc per minute, can be selected by using one or both sides of the badge. Each side has an impervious cover over the porous badge.

To analyze for contaminants, the charcoal strip is removed and placed in a vial containing a set amount of solvent (e.g. carbon disulfide). The solvent extracts the contaminants from the charcoal strip, and analysis is performed by conventional gas chromatography. The manufacturer claims this badge to be virtually independent of pressure effects and that it is only slightly affected by temperature and ambient air velocity.

Depending on the organic contaminants adsorbed by the charcoal, the sampling range varies between 0.2 ppm-hour and 2000 ppm-hours. The desorption efficiency for common vapors, such as benzene, toluene, and carbon tetrachloride, is between 95 and 100 percent. Larger molecules, e.g., more polar compounds, such as acrylonitrile, show smaller desorption efficiencies, but they are well within NIOSH requirements and give reproducible results. The passage of the vapors through the pores is controlled strictly by molecular diffusion, and diffusion coefficients of various vapors duplicate the accepted literature values for these vapors (62). The detection limit claimed for benzene is 0.20 - 0.25 ppm (64).

The Abcor Gasbadge is 6.5 cm long, 5.1 cm wide, and 1.6 cm thick. It weighs approximately 43 g and consists of seven parts: the sliding cover; the front plate of the badge, which has a 4.4 cm x 3 cm opening to allow diffusion of gases; a protective screen; a draft shield; an open grid that defines the diffusion geometry; the collection element (activated carbon); and the back plate of the badge. The Gasbadge is reusable by replacing the collection element. This dosimeter, which comes in two sizes, also relies on the ability of charcoal to selectively adsorb organic vapors and collection of the vapors by molecular diffusion rather than by mechanical means. The charcoal is solvent extracted and the extractant analyzed with a gas chromatograph. The Gasbadge specifications claim: sampling time - 8 hr nominal; sampling range - 0.2-160 ppm/8 hr TWA (benzene); accuracy - ± 25 percent at 0.2 ppm for benzene (65,66); shelf-life - 2 years.

The 3-M Organic Vapor Monitor is an oblong badge which is 10.2 cm long (including the clip), 4.4 cm wide at its widest point, and 1.2 cm thick. The sampling opening is circular with a 3 mm diameter. This badge weighs 13.5 g. During sampling, the unit consists of six pieces: the outer rim; the draft shield, which is held in place by the outer rim; an open grid that defines the diffusion geometry; the collection element; and the solid back piece of the monitor. The sixth piece is a clip for attachment to the person. The 3-M passive monitor allows for *in situ* sample elution. The Aldrich Chemical Company, Inc. (Milwaukee, Wisconsin) is a sale representative for the 3-M Organic Vapor badge.

The MiniMonitor, which was developed by Philip West at the Louisiana State University, is a circular badge. Its diameter is 5.0 cm, it is 0.625 cm thick and weighs 35 g. A feature unique to the MiniMonitor is that the badge works on the principle of permeation of contaminant gases through a membrane, followed by adsorption of the pollutant(s) onto approximately 1.35 g of PCB activated charcoal. The MiniMonitor case is reusable by introducing a fresh supply of charcoal.

CONCLUSIONS

The minimum detection limits of badges with activated carbon adsorbents could be reduced into the parts-per-billion range (10-20 ppb) by increasing sampling rate by a factor of two or more. Also, the sensitivity of charcoal badges may be improved considerably by eliminating or reducing the background adsorption, i.e., trace impurities adsorbed prior to sampling.

NIOSH is planning to look further into the use of passive monitors by testing different solid sorbents as the collection element and perhaps evaluating electrochemical detection techniques. As far as their application to ambient personal monitoring goes, the available passive monitors have some major drawbacks: 1) the monitors generally lack specificity (a drawback of some other sampling techniques as well); and 2) the detection limits of the monitors--at the low end of the scale--may not meet the needs of ambient sampling. While it is true that collection on the element is an enrichment step, it could take a long time to accumulate a detectable sample from ambient air. With certain new products that are coming out, (e.g., porous beads or porous polymers) and as the technology (e.g., electrochemical detection) allows us to develop more effective procedures, passive monitoring should be feasible in the ambient atmosphere.

SECTION 5

SUMMARY OF RECENT ACTIVITIES

The literature survey in Section 4 and the discussion on commercially available samplers is almost totally concerned with personal exposure sampling in the work-place atmosphere. Pollutant concentrations of concern are in the part-per-million range (ppm) and the best minimum detectable limits for the samplers discussed above are a few tenths of a ppm for 8-24 hour sampling. It is obvious from Section 2 (see Table 1) that the concentrations of individual toxic organic compounds in ambient air will be in the part-per-trillion (ppt) range or 2-3 orders of magnitude less than in the work-place atmosphere. Since the pumping speeds available would be about the same for ambient personal sampling as work-place sampling, the total amount of sample collected for the ambient case would be 2-3 orders of magnitude less than for work-place sampling. We can expect then that there will be quite different and/or more difficult problems associated with ambient sampling. The published literature yields little information on personal sampling for toxic organics in the atmosphere. There is some, as yet unpublished, information on recent activities in personal sampling for organics which is discussed below.

For the past two years, the Monsanto Corporation has conducted a research program to develop a portable, miniature, sorbent-based sampler and the associated analytical technology for the purpose of assessing individual exposure to toxic (primarily carcinogenic) compounds (67,68). The program consists of three phases: 1) evaluation and selection of sorbent materials and sampler design; 2) laboratory development of a prototype sampler and development of analytical methodology, which is capillary gas chromatography/mass spectrometry (GC/MS); and 3) field evaluation of the system in selected urban areas. The first two phases of this program are essentially complete.

From a survey of a wide variety of commercially available sorbent materials 1) porous polymers, e.g., Tenax-GC, Poropak, Chromosorbs; 2) carbonaceous materials, e.g., activated carbons, Ambersorbs, and 3) others, e.g., molecular sieves, silica gel, five were selected by Monsanto for detailed evaluation. These five were Tenax-GC, Poropak-N, Poropak-R, Ambersorb XE-340, and SKC activated charcoal. These five were selected because they have the potential to sample compounds which have a wide range of polarities and volatilities. These sorbents were evaluated with a matrix of 18 organic test compounds representing a wide range of volatilities, polarities and functionalities. With these compounds the 5 sorbents were evaluated with respect to capacity, desorption efficiency (thermal desorption), background, decomposition and pressure drop. The three sorbents finally selected were Tenax-GC, Poropak-R, and Ambersorb XE-340 for the collection of low volatility, intermediate volatility and high volatility compounds, respectively.

Poropak-R was chosen over Poropak-N because it gave a much better background in the GC/MS analysis. Ambersorb XE-340 was chosen because of "less difficulty anticipated with desorption and fewer detrimental effects by water and reactivity with collected samples (68).

The sampler designed by Monsanto consists of three tapered glass tubes, each containing 1-2 grams of the sorbent, arranged in series, followed by a flow control device and ending with a portable miniature pump.

Considerable progress has also been made in developing the associated GC/MS analytical technology. The Monsanto personnel have estimated detection limits of 1-10 ppt for a variety of organic compounds for a 480 liter sample (1 L/min. for 8 hr.). This is based on an assumed detection limit of 10 nanograms (ng) for capillary column GC/MS (69).

Pellizzari has reported favorable results with the use of Tenax-GC as the sorbent in a glass tube sampler for a wide variety of organic compounds which may be present in ambient air (43,70, 71). Among the advantages of Tenax-GC were high collection efficiencies, good thermal desorption efficiencies with low attendant background up to 300 °C, the absence of any effects from variable atmospheric humidity, and good storage properties. The only apparent drawback is low capacity or low breakthrough volume (in liters air per gram of sorbent) for highly volatile organics. Compounds with a vapor pressure greater than about chloroform (b.p. = 61 °C) can not be collected efficiently. This would rule out Tenax-GC for the collection of compounds such as methyl chloride and dichloromethane, which are on the TSCA Priority List.

Activated carbons should have the efficiency required for the collection of the highly volatile organics (68). However Pellizzari reports (71), and the Monsanto report (68) implies, that quantitative thermal desorption cannot be achieved for ambient samples of organics on activated carbons. Solvent desorption may work for the activated charcoals, and this is the technique commonly used in NIOSH procedures. However, the amount of any individual ambient organic collected in a miniature sampler will be small for a normal sampling volume, e.g., 1-100 ng. Elution of this amount would result in a very dilute solution of a very volatile organic and quantitative concentration of the solution would be difficult. Since only an aliquot of this dilute solution could be used for the GC analysis, the overall sensitivity of the method would be reduced to the point that may probably be inadequate for ambient analysis. Brooks and West (72) have recently encountered just this problem in attempting to analyze for a number of volatile organics adsorbed on Ambersorb XE-340 by solvent extraction.

We are aware of only two field studies utilizing miniature personal samplers. The first is an unpublished study by Pellizzari, et al. (73). This study utilized a glass tube cartridge with Tenax-GC as sorbent and a MSA miniature pump for the personal sampling of benzene in St. Louis and Houston. The results of this study showed ambient levels of benzene in St. Louis which could be correlated with source activities and ubiquitous levels of benzene in the Houston area. The EPA TEAM study mentioned earlier has employed the same personal samplers to measure 8-hour exposures of students at Lamar

University in Texas and the University of North Carolina and also of the general public in Research Triangle Park, N.C., and Elizabeth and Bayonne, N.J. A dozen or more organic compounds were detected, with concentration levels ranging from 0.1 to 100 ppb.

There have been several other recent field studies on ambient volatile organics in which personal samplers were not used, but which are pertinent to this report. An EPA study in Dallas, Chicago, and Los Angeles (74) utilized a Tenax-GC sorbent, thermal desorption and GC-flame ionization analysis to measure ambient concentrations of benzene. Levels observed were 5 $\mu g/m^3$ (1.6 ppb) for Dallas, 18 $\mu g/m^3$ (5.6 ppb) for Chicago and 19 $\mu g/m^3$ (6.0 ppb) for Los Angeles.

Another EPA study in New York City, Houston and Detroit utilized an activated carbon sorbent, solvent elution with carbon disulfide and GC-electron capture detection for the measurement of ambient levels of tetrachloroethylene (75). All the measurements in New York City gave values greater than 0.1 ppb (the minimum detection limit), one-half were greater than 1 ppb, and the maximum value observed was 10 ppb. In Houston and Detroit, 90 percent of the measurements gave values less than 1 ppb. If these results are valid, they would contradict the earlier statements on recovery from charcoal and inadequate sensitivity using solvent extraction. With regard to sensitivity these results may reflect the much greater sensitivity of electron capture as opposed to flame ionization detection. We have already alluded to the recent EPA study (24) in Houston, Niagara Falls, Newark, and New Orleans in which volatile chlorinated organics and benzene were consistently found. This study utilized 2 1/2 grams Tenax-GC in a glass tube sampler, collection of ca. 100 liters total sample, thermal desorption and GC/MS analysis.

SECTION 6

RECOMMENDATIONS FOR RESEARCH AND DEVELOPMENT OF ACTIVITIES

We have presented below our concepts of all the major research and development needs in the field of personal monitoring for toxic organics. We would recommend top priority for the nine organics from column 3, Table 3 as well as methyl and methylene chloride from the TSCA priority list. With the exception of benzene, these represent a single class of compounds - volatile chlorinated organics with long atmospheric persistence. This also presents the possibility of using highly sensitive electron capture (EC) detection, again with the exception of benzene, in the GC analysis. This could lead to greatly reduced requirements in terms of amount collected for many of these compounds.

Research and development activities on personal monitoring for volatile chlorinated organics are recommended in the following areas:

1. Evaluation of sorbent materials

2. Development of analytical techniques based gas chromatography with electron capture and photoionization detection.

3. Evaluation of active samplers

4. Development and evaluation of passive samplers

5. Development of standard mixtures for evaluation and calibration of personal exposure devices.

Tenax-GC has been shown to be an excellent sorbent for a wide variety of organic compounds and exhibits such desirable properties as good collection efficiencies, high operating temperature (350 °C) for thermal desorption, with low background bleeding and a low retentive index for water (43). However we have seen little documentation on the use of Tenax-GC for the collection of the particular chlorinated compounds discussed above. Therefore Tenax-GC should be evaluated on these compounds with respect to collection efficiency, breakthrough volume and thermal desorption efficiency. Brooks (76) reported a low breakthrough volume (< 1 L/g) for CCl_4. As indicated earlier, Tenax-GC would probably be inefficient for the collection of the more volatile chlorinated organics such as chloromethanes. Other sorbents should be evaluated such as Chromosorb 104, as suggested by Pellizzari (43), or Poropak-R (68). Another possibility would be to attempt to develop a porous polymer analogous to Tenax-GC, but with a greater capacity for highly volatile compounds.

Activated carbons and the carbonaceous material Ambersorb XE-340 should collect the volatile chlorinated compounds, but thermal desorption is not feasible for activated carbons and more work is required to determine desorption efficiencies for Ambersorb XE-340. Some effort should be made to study solvent desorption efficiency and to determine whether EC-GC would have the required sensitivity with the resulting solutions.

Because of the inherent high sensitivity, EC-GC techniques should be developed for the analysis of the chlorinated organics. Detection limits in the range of 10^{-12} to 10^{-14} g are possible with EC detection (69). If a chlorinated compound (M.W. = 100) with an atmosperic concentration of 1 ppt is sampled at a rate of 1 L/min. for 8 hours (ca. 500 liters), the amount of sample collected will be 2×10^{-9} g. If quantitative thermal desorption is possible, this sample weight is still well above detection limits. On the other hand, it would be well below the detection limits by flame ionization. Since many chlorinated compounds are likely to be found in the ambient atmosphere, the principal problem expected is chromatographic resolution. This is an area which may require the most effort in terms of analytical technique development. Recent developments in fused silica capillary column technology should be investigated for improved resolution. The use of flame ionization detection (FID) is likely the best approach for benzene and some of the other chlorinated compounds with concentrations of 0.1 ppb or greater. Photoionization detectors would provide greater sensitivity and applicability to a broad range of organic compounds and should be evaluated.

Active sampling devices have been developed which may be amenable to personal exposure studies. Pellizzari (73) has used a personal Tenax-GC sorbent sampler in the field, and a multiple sorbent sampler has been developed by Monsanto (69). These samplers should be evaluated with volatile, chlorinated organics with respect to collection efficiency, breakthrough volumes, desorption efficiencies and tested under realistic field conditions.

The development of passive sampling devices for toxic organics at ambient levels is a largely unexploited area and should be of considerable interest in a longer out-put time frame. We are currently investigating some promising passive samplers for inorganic air pollutants at ambient levels (77) and this technology should be applicable to the toxic organics. The primary advantage of passive samplers is in their size, and possibly cost, in that no pumps or other moving parts are required. The key to developing an effective ambient passive sampler is in attaining a high equivalent passive sampling rate. As discussed in the report on passive samplers for NO_2 (77), this equivalent sampling rate (F_{eq}) is determined by the diffusion rate of the pollutant to the collection medium and by sampler geometry,

$$F_{eq} = D \times A/\ell$$

where D = diffusion coefficient, cm^2/s

A = area of diffusion barrier, cm^2

ℓ = length of diffusion barrier, cm.

Since the diffusion rate is constant for a particular diffusion medium and pollutant, the sampling rate is strongly controlled by the geometry term, A/ℓ, which can conceivably be made quite large. For a passive membrane NO_2 sampler we are evaluating, the diffusion barrier is a thin circular silicone membrane with an A/ℓ of ca. 500 (77). Other designs could conceivably further increase this value. For example, a double sided membrane sampler with substrate in between would double this value. A multilayered membrane sampler may increase this rate by the number of layers. There are certainly other design geometries whereby high area, thin film barriers can be structured within a small personal sampler, and this is an area which should be explored. Some of the commercially available work place badge samplers have sampling rates of 30-100 cm^3/min. With a more creative design, sampling rates equivalent to that of available miniature pumps (1 L/min.) should be feasible.

There remains the question of the feasibility of using commercially available dosimeter badges (Abcor, 3-M, Dupont) for sampling and analysis of the volatile chlorinated organics. However, these badges use activated charcoal as sorbent (the NIOSH method) and thermal desorption and direct injection into the gas chromatograph apparently cannot be done with any efficiency (68, 71). The NIOSH work place methods use solvent elution, but much larger quantities of adsorbed pollutant are available. Nevertheless, we should consider the case of elution of a typical chlorinated organic from charcoal for EC-GC analysis.

Let us assume a hypothetical case using best estimates. A passive badge with an equivalent sampling rate of 75 cm^3/min. (a high value) would sample 100 liters of air in a 24 hour period. For a light chlorinated compound (e.g., mw $\sim$ 100) at a concentration of 100 ppt (0.1 ppb), 4×10^{-8} g would be adsorbed if the efficiency is 100 percent. Let's assume that this compound can be eluted efficiently with 4 mL of solvent (a typical value) to yield a solution with a concentration of 10^{-8} g/mL or 10^{-5} µg/µL. Injection of 1 µL (a normal value) of this solution into the chromatograph corresponds to 10^{-11} g of the chlorinated compound. The detection limits of modern GC instruments for chlorinated compounds are in the range of 10^{-12} - 10^{-14} g. Therefore the compound should be detectable. There were several assumptions made above, but this simple analysis does demonstrate that the commercial badges should at least be evaluated for the volatile chlorinated compounds with EC-GC analysis.

With regard to standard mixtures, NBS is already in the process of developing standards for some of these chlorinated compounds (see Table 3). These standards and the generation systems employed should be useful in the evaluation and calibration of sampling devices considered here. Both cylinder standards and permeation tube devices are being developed for the compounds listed in column 4 of Table 3.

REFERENCES

1. Wallace, L. Personal Air Quality Monitors: Past Uses and Present Prospects. In: Proceedings of the 4th Joint Conference on Sensing of Environmental Pollutants. American Chemical Society, Washington, D.C., 1978, p. 109A.

2. a. Butcher, S. S., and R. J. Charlson. An Introduction to Air Chemistry. Academic Press, New York, 1972.

   b. Bailey, R. A., H. M. Clark, J. P. Ferris, S. Krause, and R. L. Strong (eds.) Introduction to Chemistry of the Environment. Academic Press, New York, 1978.

3. Leighton, P. A. Photochemistry of Air Pollution. Academic Press, New York, 1961.

4. Heicklen, J. Atmospheric Chemistry. Academic Press, New York, 1976.

5. Molina, M. J., and F. S. Rowland. Nature (London), 249:810, 1974.

6. Cicerone, R. J., R. S. Stolarski, and S. Watters. Science, 185:1165, 1974.

7. Crutzen, P. J. Geophys. Res. Lett., 1:205, 1974.

8. Interdepartmental Committee for Atmospheric Sciences. The Possible Impact of Fluorocarbons and Halocarbons on Ozone. ICAS 18A-P5, National Science Foundation, Washington, D.C., May 1975.

9. National Emissions Standards for Vinyl Chloride. Federal Register, 41: 46559, Oct. 21, 1976.

10. National Emission Standards for Hazardous Air Pollutants — Addition of Benzene to List of Hazardous Pollutants. Federal Register, 42(110): 29332, June 8, 1977.

11. Standard Support and Environmental Impact Statement Vol. 2: Promulgated Emission Standard for Vinyl Chloride. EPA-450/2-75-0096. Office of Air Quality Planning and Standards. Environmental Protection Agency, Research Triangle Park, NC, September, 1976.

12. Health Effects of Benzene: A Review. National Academy of Sciences, Washington, D.C., June, 1976.

13. Leukemia Among Workers Exposed to Benzene. National Institute for Occupational Safety and Health, Cincinnati, Ohio, April, 1977.

14. Graedel, T. E. Chemical Compounds in the Atmosphere. Academic Press, New York, 1978.

15. The Clean Air Act. 42 U.S.C. 7401 et seq. As amended by the Air Quality Act of 1967. PL 90-148. Clean Air Amendments of 1970. PL 91-604. Clean Air Amendments of 1977. PL 95-65.

16. Toxic Substances Control Act. 15 U.S.C. 2601 et seq. PL 94-469, October 12, 1976.

17. National Primary and Secondary Air Quality Standards. Federal Register, 36(84):8186, April 30, 1971.

18. Helms, L. H., K. D. Reiszner, and P. W. West. Anal. Chem., 49:994, 1977.

19. West, P. W., and K. D. Reiszner. Amer. Ind. Hyg. Assn. J., 39:645, 1978.

20. a. Toxic Substances Control Source Handbook. A. McRae, L. Whelchel, and H. Rowland (eds.) The Center for Compliance Information. Aspen Corp., Germantown Md., 1978.

    b. Christenson, H. E. (ed.) Toxic Substances List. 1973 Edition. NIOSH, Rockville, Md., 3, 1973.

21. McMillan, C. R., L. B. Mate, and D. C. DeAngelio. Identification, Sampling, and Analysis of Atmospheric Carcinogens Using Multiple Sorbents. Report to the Environmental Protection Agency, Environmental Science Research Laboratory (James Mulik - Project Officer), Research Triangle Park, NC, Dec. 1978.

22. Atkinson, R., K. D. Darnell, C. C. Lloyd, A. Winer and J. N. Pitts, Jr. Advances in Photochemistry., 11:375, 1979.

23. Reaction Rate and Photochemical Data for Atmospheric Chemistry — 1977. R. F. Hampson, Jr., and D. Garvin (eds.) NBS Special Publication 513. National Bureau of Standards, Washington, D.C., 1978.

24. a. Pellizzari, E. D., M. D. Erikson and R. A. Zweidinger. Formulation of a Preliminary Assessment of Halogenated Organic Compounds in Man and Environmental Media, EPA-560-13-79-000, 1979.

    b. Pellizzari, E. D., et al., Preliminary Study of the Toxic Chemicals in Environmental and Biological Media — Part I., Report to the Environmental Protection Agency, Office of Research and Development (Lance Wallace - Project Officer) Washington, D.C. 20460, 1980.

25. Butler, J. D., and P. Crossley. Sci. Total Environm., 11:53, 1979.

26. Environmental Quality. The annual reports of the Council on Environmental Quality. U.S. Government Printing Office, 1970 ff.

27. Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents. National Institute for Occupational Safety and Health. HEW Publication No. (NIOSH) 75-184. U.S. Government Printing Office, Washington, D.C., 1975.

28. Linch, A. L. Evaluation of Ambient Air Quality by Personal Monitoring. CRC Press, Inc., West Palm Beach, Florida, 1974.

29. Melcher, R. G., R. R. Langner, and R. O. Kagel. Amer. Ind. Hyg. Assoc. J., 39:349, 1978.

30. Bursey, J. T., D. Smith et. al. American Laboratory (Fairfield, Conn.) 9:35, 1977; Chem. Abstr. 89:168178a.

31. Ballou, E. V. (ed.) Second NIOSH Solid Sorbents Roundtable. NIOSH, HEW Publication, Cincinnati, Ohio, 1976; Chem. Abstr. 86:194144j.

32. Mage, D. I. and L. A. Wallace (eds.), Proceedings of the Symposium on the Development and Usage of Personal Monitors for Exposure and Health Effect Studies. EPA-600.9-79-032, June, 1979.

33. National Institute of Occupational Safety and Health: NIOSH Manual of Analytical Methods. HEW Publication No. (NIOSH) 77-157, Cincinnati, Ohio, 1977.

34. Brooks, J. J., D. S. West, D. J. David, and J. D. Mulik. A Combination of Sorbent System for Broad Range Organic Sampling in Air. Ref. 32, p. 383.

35. Melcher, R. G., R. R. Langer, and R. O. Kagel. J. Amer. Ind. Hyg. Assoc., 39:349, 1978.

36. Gallant, R. F., J. W. King, P. L. Levins, and J. F. Piecewicz. Characterization of Sorbent Resins for Use in Environmental Sampling. EPA-600/7-78-054, March, 1978, pp. 79-92.

37. Holzer, G., H. Shanfield, A. Zlatkis, W. Bertsch, P. Juarez, H. Mayfield, and H. M. Liebich. Collection and Analysis of Trace Organic Emissions from Natural Sources. J. Chromatogr., 142:755-764, 1977.

38. Dietrich, M. W., L. M. Chapman, and J. P. Mienre. Amer. Ind. Hyg. Assoc. J., 39:385, 1978.

39. Ciccioli, P., G. Bertoni, E. Brancaleoni, R. Fratarcangeli, and F. Bruner. J. Chromatogr., 126:757, 1970.

40. Dorigen, J., B. Fuller, and R. Duffy. U.S. NTIS, PB Rep. ISS PB-264446, 1976, p. 312-336; Chem. Abstr. 87:140410e.

41. Raymond, A., and G. Guiochon. J. Chromatog. Sci., 13:173-177, 1973.

42. Mieure, J. P., Ref. 31, pp. 121-138.

43. Pellizzari, E. D., J. E. Bunch, R. E. Berkley, and J. McRae. Analytical Letters, 9(1):45-63, 1976.

44. Whitmore, F. C., R. L. Durfee, and M. N. Khattak. EPA Contract 68-02-2618, NTIS-PB 279672. Versar, Inc., Springfield, Virginia, 1977; Chem. Abstr. 89:220155g.

45. Bursey, J. T., D. Smith et. al. American Laboratory, 9:35, 1977; Chem. Abstr. 89:168178a.

46. Butler, J. D. Air Pollution., Academic Press, London, 1979.

47. Federal Register. 39(194):35890, October 4, 1974.

48. Zlatkis, A., H. A. Lichtenstein, and A. Tishbee. Chromatographia, 6:67, 1973.

49. Bamberger, R. L., G. G. Esposito, B. W. Jacobs, G. E. Podolak, and J. F. Mazur. Amer. Ind. Hyg. Assoc. J., 39:701, 1978.

50. Dravnieks, A., B. K. Krotaszynski, J. Barton, A. O'Donnell, and J. Burgwald. High Speed Collection of Organic Vapors from the Atmosphere. In: The 11th Conference on Methods in Air Pollution and Industrial Hygene Studies, Berkely, California, 1970.

51. Instrumentation for Environmental Monitoring. AIR, Vol. 1, LBL 1. Environmental Instrumentation Group. Lawrence Berkeley Laboratory, Berkeley, California, 1973.

52. Instrumentation for Monitoring Air Ouality. ASTM Spec. Tech. Publ. 555. American Society for Testing and Materials, Philadelphia, 1974.

53. Harrison, J. W., D. E. Gilbert, P. A. Lawless, and J. H. White. Development Strategy for Pollution Dosimetry. Research Triangle Institute. Research Triangle Park, North Carolina, 1975.

54. Strupp, P. E., P. M. Jones, R. D. Giammar, and T. B. Stanford. Intern. Confer. Environmental Sensing and Assessment. Las Vegas, Nevada, 1975, 2:22-23; Chem. Abstr. 86:95285k.

55. Morgan, M. G., and S. C. Morris. Assessment of Research Needs in Individual Air Pollution Monitors for Ambient Air. Bookhaven National Laboratory, Upton, New York, 1976.

56. Harrison, J. W., D. E. Gilbert, P. A. Lawless, J. H. White, and A. E. O'Keeffe. Development Strategy for Pollutant Dosimetry. EPA-600/2-2-76-03, February, 1976.

57. Assessment of Benzene as a Potential Air Pollution Problem. Vol. IV, GCA/Technology Division, Bedford, Massachusetts. Prepared for Environmental Protection Agency, Research Triangle Park, North Carolina 27711. Publication No. EPA-PB-758 356, January 1976.

58. West, P. W. Toxicology Research Projects Directory. Vol. 4, issue 06, 1979; SSIH/IOH 666B.

59. Cralley, L. V., and L. J. Cralley (eds.) Hygiene and Toxicology Vol III: Theory and Rational of Industrial Hygiene Practice. Wiley-Interscience, New York, N.Y., 1979.

60. a. Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents. National Institute for Occupational Safety and Health. HEW Publication No. (NIOSH) 75-184. U.S. Government Printing Office, Washington, D.C., 1975.

b. Cadoff, B. C., B. Greifer, P. A. Pella, and J. K. Taylor. Development of Contaminant Generation Systems for Certification of Portable Air Sampling Instruments. National Bureau of Standards, Washington, D.C., 1975.

61. Woebkenberg, M. L., in Ref. 32, pp. 7-8.

62. Pro-Tek Organic Vapor G-AA Air Monitoring Badge No. 1. Technical Bulletin, 1979. E. I. Dupont De Nemours and Company, Inc., Applied Technology Division, Wilmington, Del. 19898.

63. Chemical and Engineering News. 57(2):21, July 9, 1979.

64. Frick, R. A., and Graig Schukert. DuPont Applied Technology Division, Personal Communication, Tel: (302) 774-7458.

65. Gasbadge, Organic Vapor Dosimeter. Technical Bulletin 1979. Abcor Development Corporation, 850 Main Street, Wilmington, MA 01887.

66. Leah, D. Abcor Development Corporation, 850 Main Street, Wilmington, MA 01887. Personal Communication, Tel: (617) 657-4250.

67. DeAngelio, D. G., A. G. Desai, and C. R. McMillan. Methods for the Sampling and Analysis of Organic Materials — State-of-the-Art. Draft report to the Environmental Protection Agency, Research Triangle Park, NC. Contract No. 68-02-2773, January, 1979.

68. Brooks, J. J., and D. S. West. Portable Collection System and Analytical Technology for Atmospheric Carcinogen Assessment. Draft Report to the Environmental Protection Agency, Research Triangle Park, NC. Contract No. 68-02-2774, October, 1978.

69. Diard, D. J. Gas Chromatographic Detectors. John Wiley, & Sons, New York, 1974.

70. Pellizzari, E. D., J. E. Bunch, and B. H. Carpenter. Envir. Sci. Tech., 9(6):552, 1975.

71. Pellizzari, E. D., B. H. Carpenter, and J. E. Bunch, ibid., p. 556.

72. Brooks, J. J., and D. S. West. Development of a Portable Miniature Collection System for the Exposure Assessment within the Microenvironment for Carcinogens, Precarcinogens and Cofactors. 23rd Monthly Progress Report. Contract No. 68-02-2774. Environmental Protection Agency, Research Triangle Park, NC, August, 1979.

73. Private communication. Pellizzari, E. D. Research Triangle Institute, Research Triangle Park, NC.

74. Martin, B. E., T. Clark and J. Bumgarner. Ambient Air Monitoring for Benzene - 24 Hour Integrated Sampling in Six Cities. Draft Report. Environmental Monitoring Systems Laboratory. Environmental Protection Agency, Research Triangle Park, NC, 1980.

75. Evans, G. F., R. E. Bumgardner, J. E. Bumgarner, P. L. Finkelstein, J. E. Knoll, and B. E. Martin. Environmental Protection Agency. And G. L. Sykes, D. E. Wagoner, and C. E. Deckor. Research Triangle Institute. Measurement of Perchloroethylene in Ambient Air. EPA-600/4-79-047. Environmental Monitoring and Support Laboratory. Environmental Protection Agency, Research Triangle Park, NC, August, 1979.

76. See Reference 73. 20th Monthly Progress Report. May, 1979.

77. Cadoff, B. C., S. F. Knox, and J. A. Hodgeson. Personal Exposure Samplers for Nitrogen Dioxide. Draft Report. NBS-EPA Interagency Agreement No. AD-13-F-0-034-0. National Bureau of Standards, Washington, D.C., November, 1979.